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Edward Chung-Hong Liu

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THE ANODIC DISSOLUTION OF TIN IN ACIDIC CHLORIDE SOLUTIONS

BY

EDWARD CHUNG-HONG LIU, 1940-

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THESIS

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Approved by

James W. Johnson (Advisor)

W. J. James

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THE ANODIC DISSOLUTION OF TIN IN ACIDIC CHLORIDE SOLUTIONS

Edward Chung-hong Liu

Department of Chemical Engineering and
Graduate Center for Materials Research

University of Missouri-Rolla

Rolla, Missouri, U.S.A.

Abstract

The anodic dissolution of Sn in acidic chloride solutions (pH = -2.0 to 2.9) was studied at 25°C. The apparent valence of the dissolving ions varied from about 0.4 to 2.4, a function of both electrolyte and c.d. The complexing of Sn^{+2} by Cl^- had an important influence with $SnCl_3^-$ apparently being the dominant product. A reaction sequence is proposed involving the step-wise oxidation of Sn accompanied by reaction with Cl^-.

Introduction

In the absence of complexing and oxidizing agents, Sn has good stability toward aqueous solutions whose pH's range from moderately acidic to slightly basic. This stability is attributed to both a protective oxide film and a high hydrogen overpotential. Chloride ions are known for their ability to complex with Sn and make the metal susceptible to corrosion, both by breaking down the protective film and lowering the anode potential. An extensive study of their effect in nearly neutral solutions has been reported by Hoar.[1] The purpose of this study was to determine the anodic behavior of Sn in acidic chloride solutions. In such solutions, passivation by oxide film formation should be at a minimum which allows one to examine the anodic dissolution process.

Experimental

Cylindrical Sn specimens were cut from rods cast from bars of 99.999% minimum purity.* They were wet - polished on grinding paper down to grit 600, rinsed with distilled water, dried in a desiccator, and mounted in a Teflon holder to complete the anode assembly.[2] All solutions employed analytical grade chemicals and distilled water. The electrolyses were carried out in the usual H-cell (300 ml capacity) at 25 ± 0.1°C with a Pt cathode. The reference electrode was Hg/Hg_2Cl_2 (1 N KCl) and was connected to the anode via a Luggin capillary and salt bridge of the same electrolyte as used in the electrolysis cell. All potentials reported are versus the standard hydrogen electrode (SHE) at 25°C and have been corrected

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*Electronic Space Products, Inc. 5 N grade (99.999% min. purity).

for junction potentials. Prepurified nitrogen was bubbled through the electrolyte to provide an inert atmosphere and for stirring.

The amounts of Sn dissolved were determined by a direct weight-loss method. The anodic polarization behavior was determined both galvanostatically and potentiostatically. Reasonably steady states (less than 10% change per hour) were obtained in all cases except as noted.

Results

Valence Measurements. The results of valence measurements are shown in Tab. I. The individual values were reproducible within ±2%. In the more acidic electrolytes (pH $\leq$ 0.2), a black film was present on the anode surface which spalled off at high c.d.'s. An examination of the spalled film showed it to contain small metal particles as reported previously by Straumanis.[3] For these solutions, the apparent valences were lowest at the lower c.d.'s and approached the expected value of two as the current was increased. In 10 N HCl, there was substantial self-dissolution of the Sn as evidenced by H_2 evolution at local cathodic sites and also pitting during anodic dissolution. No pitting occurred in the other solutions.

In the solutions of higher pH (1.2 - 2.9) the apparent valences were ca. 2 or slightly greater. In 0.1 N HCl - 0.9 N KCl, the anode surface retained its metallic appearance at low c.d.'s. In the other solutions, a black film was initially formed that slowly turned gray. X-ray diffraction analyses of the films yielded lines associated primarily with SnO and $2SnO \cdot H_2O$. No gas (O_2) evolution was noted, even at the high c.d.'s, and no Cl_2 was detected in the anolyte after the electrolyses.

When apparent valences greater than +2 were obtained, small quantities of Sn-IV were detected in the anolyte along with Sn-II. For all the other cases, only Sn-II was found.

Polarization Measurements. The rest potentials of the Sn electrode in various solutions are also shown in Tab. I. Steady values were obtained in about 20 minutes that remained quite stable for several hours. Anodic polarization experiments were performed in the same electrolytes as the valence measurements and the resulting curves are shown in Fig. 1. There were linear Tafel sections in the region slightly more positive than the rest potentials. No passivation was found for the electrolytes $pH \leq 1.2$, though limiting (potential independent) currents were found that showed no simple concentration dependence. The commencing of this latter type of behavior appeared to be potential dependent.

With the electrolytes $pH = 2.2$ and 2.9, significantly decreased currents with increasing potential were obtained above a critical potential. An inspection of the data from the previous section shows that this is only "quasi" passivation and that Sn dissolution is the predominant reaction at this and even higher c.d.'s. The critical currents are apparently pH dependent as the Cl^- concentration was constant in these solutions. The quasi-passivation commenced at potentials of -0.25 to -0.20 v.

Discussion

The apparent valences of the Sn ions determined from coulombic data lie both above and below the expected value of +2. The lower values occur in the electrolytes of lower pH and at the lower c.d.'s. They are consistent with anodic dissolution that is accompanied by self-dissolution (local corrosion). In the extreme case, (10 N HCl, i = 0), spontaneous dissolution was quite rapid. This process is undoubtedly assisted both by the increased H^+ concentration and the ability of Cl^- to complex with Sn^{+2}, thereby lowering the local anode potential and also removing any surface film, so that H_2 can be evolved. The rate of local corrosion does not appear to be greatly affected by the impressed current, hence, the increase of valence with current density. This is consistent with local corrosion that is not film controlled. It is also consistent with proposals that anodic disintegration results from a combination of normal anodic dissolution and local corrosion.[2,3]

In the intermediate pH range (0.2-2.2), the apparent valences do not deviate from the normal value of +2 by more than ± 10%. This deviation is outside the limit of experimental error and while the normal oxidation of Sn to Sn-II is the dominant reaction, it is not the exclusive one.

At pH = 2.9, values were obtained that are significantly higher than +2. Analyses of these anolytes revealed that Sn-IV was produced as well as Sn-II. At lower pH's only Sn-II was detected. Considering this and the absence of oxygen evolution, the increased valence is accounted for by the further oxidation of some of the Sn-II to Sn-IV or the direct oxidation of Sn to Sn-IV.

An examination of the rest potential data pH = 0.2 - 2.9 ($C_{Cl^-} = 1.0$ N) from Tab. I shows them to be essentially pH independent, i.e., $\partial V_{rest}/\partial pH \approx 0$.* The rest potentials for the remaining solutions where both pH and C_{Cl^-} are changing are seen to decrease with increasing Cl^- concentration. A plot of these values vs. the corresponding Cl^- activity is shown in Figure 2.** A reasonable

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*Also note the rest potentials reported by Hoar (Ref. 1) for KCl solutions (pH=7). They differ from the corresponding values in this study by only about 60 mv while the pH has changed by 6-9 units.

**The Cl^- activities were calculated using the mean ionic activity coefficients from Refs. 4 and 5.

linear relationship is obtained in which $\partial V_{rest}/\partial \log a_{Cl^-} \approx -0.085v$. The decrease in potential can be explained in terms of the complexing ability of Cl^- for Sn^{+2} and the variation can be used to estimate the extent of complexing from the reactions

$$Sn(s) = Sn^{+2}(sol) + 2e \tag{1}$$

$$Sn^{+2}(sol) + x\,Cl^-(sol) = (SnCl_x)^{+2-x}(sol) \tag{2}$$

Combining the Nernst equation for eq. 1*

$$E = -0.136 + 0.0295 \log a_{Sn^{+2}} \tag{3}$$

and the equilibrium relation for eq. 2

$$K_2 = \frac{a_{(SnCl_x)^{+2-x}}}{a_{Sn^{+2}}\,a^x_{Cl^-}} \tag{4}$$

gives

$$E = -0.136 + 0.0295\,(pK_2 - x\log a_{Cl^-} + \log a_{(SnCl_x)^{+2-x}}) \tag{5}$$

The partial derivative with respect to $\log a_{Cl^-}$ of this expression gives

$$\partial E/\partial \log a_{Cl^-} = -0.0295x \tag{6}$$

Assuming the measured rest potentials are the reversible values corresponding to eq. 5, then

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*For the reduction potential.

$$\partial E/\partial \log a_{Cl^-} = \partial V_{rest}/\partial \log a_{Cl^-} \qquad (7)$$

and

$$-0.0295x = -0.085$$

or

$$x \simeq 3$$

The measured rest potentials can now be checked against the reversible values by comparing a potential from eq. 5 with a corresponding value from Fig. 2. Equilibrium constants for the formation of $SnCl^+$, $SnCl_2$, $(SnCl_3)^-$, and $(SnCl_4)^=$ from one Cl^- and the adjacent lower complex have been given by Duke and Courtney[6] as 11.3, 5.1, 0.24, and 1.0, respectively. Thus, the value for eq. 2 (x = 3) is

$$K_2 = (11.3)(5.1)(0.24) = 13.8$$

and

$$pK_2 = -1.141$$

Substituting in eq. 5 gives

$$E = -0.170 + 0.0295 \log a_{(SnCl_3)^-} - 0.0886 \log a_{Cl^-} \qquad (8)$$

When a metal is immersed in a solution that initially contains none of its dissolved species, a double-layer activity of 10^{-6} is often assumed to estimate the reversible potential. Using this value for $SnCl_3^-$ in eq. 8 gives

$$E = -0.347 - 0.0886 \log a_{Cl^-} \qquad (9)$$

From this equation for $a_{Cl^-} = 1$, $E = -0.347$v which compares to -0.32v from Fig. 2.* This is in fair agreement considering the approximations used and allows one to attribute the rest potentials to the reaction

$$Sn(s) + 3\ Cl^-(sol) = (SnCl_3)^-(sol) + 2e \qquad (10)$$

In the present study, this represents the overall electrochemical dissolution reaction.

The Tafel slopes from the linear portions of the polarization curves (Tab. I) are all approximately 30 mv, i.e., 2.3RT/2F. This value is associated with a reaction sequence that has a chemical rate determining step proceeded by two equilibrium charge transfers. A further examination of the Tafel sections also gives information about species involved in the sequence. First, these sections for pH's 1.2-2.9 almost superimpose. Since these are solutions in which $a_{Cl^-} \simeq$ constant, it appears that H^+, OH^-, or H_2O are not involved in the quasi-equilibrium steps nor H^+ or OH^- in the r.d.s. A semi-log plot of V vs. a_{Cl^-} at constant current for the solutions with varying Cl^- concentrations is shown in Fig. 3. The relationshop is reasonably linear and gives $\partial V/\partial \log a_{Cl^-} \simeq -100$ mv. A value of 90 mv would be consistent with a reaction order of 3. The reaction mechanism suggested by these results is

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*For an assumed d.l. activity of $SnCl_3^- = 10^{-5}$, the calculated and experimental values would be approximately the same.

$$Sn(s) + Cl^{-}(sol) = SnCl(s) + e$$

$$SnCl(s) + Cl^{-}(sol) = SnCl_2(s) + e$$

$$SnCl_2(s) + Cl^{-}(sol) \xrightarrow{r.d.s.} (SnCl_3)^{-}(sol)$$

The absence of passivation in the solutions $pH < 1$ is explained by the removal of protective Sn oxide (or hydroxide) films through the complexing action of the Cl^{-}. At these pH's the oxides are unstable and will not reform.[1,2] At pH's 2-3, SnO or $Sn(OH)_2$ are formed at potentials of -0.3 to -0.2 v, agreeing quite closely with the potentials at which the Sn passivates.[1] At slightly higher potentials, it is also possible to form SnO_2 or $Sn(OH)_4$, which explains the higher observed valences and the presence of Sn-IV species.[7]

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TABLE I

APPARENT VALENCE OF Sn IONS, REST POTENTIALS AND TAFEL SLOPES FOR THE ANODIC DISSOLUTION OF Sn AT 25°C

Electrolyte g-mole/l			Current Density, i x 10^{-3} amp/cm^2							Rest Potential*	Tafel Slope
HCl	KCl	pH	1	3	10	20	30	60	100	volts (SHE)	volts
10.00	-	-2.0	0.39	0.81	1.48	-	1.89	1.84	1.94	-0.481	0.024
			0.39	0.82	1.49	-	1.94	1.83	1.92		
3.00	-	-0.6	1.77	1.77	1.91	1.99	1.99	1.96	1.97	-0.351	0.027
			1.69	1.77	1.88	1.97	1.96	1.94	1.95		
1.00	-	0.2	1.79	1.82	1.82	-	1.91	1.93	1.98	-0.309	0.027
			1.82	1.79	1.82	-	1.94	2.05	1.99		
0.100	0.900	1.2	-	2.01	-	-	2.00	-	1.96	-0.310	0.027
			-	2.01	-	-	1.99	-	1.96		
0.010	0.990	2.2	-	2.07	-	-	2.05	-	2.11	-0.323	0.028
			-	1.99	-	-	2.04	-	2.08		
0.001	0.999	2.9	-	2.36	-	-	2.30	-	1.95	-0.320	0.028
			-	2.36	-	-	2.36	-	1.97		

*Corrected for junction potentials using equivalent conductance data.

CAPTIONS FOR FIGURES

1. Anodic polarization curves for the Sn electrode in acidic chloride solutions at 25°C.
   (■ , 10 N HCl; ▲ , 3 N HCl; △ , 1 N HCl; ○ , 0.1 N HCl - 0.9 N KCl; ▽ , 0.01 N HCl - 0.99 N KCl; □ , 0.001 N HCl - 0.999 N KCl; ● , 0.001 N HCl - 0.999 N KCl [galvanostatic]).

2. Rest potentials of the Sn electrode in chloride solutions at 25°C.
   (o, data from this study for HCl solutions; △, Hoar's data for KCl solutions).

3. Effect of Cl^- on the anodic dissolution of Sn at 25°C.

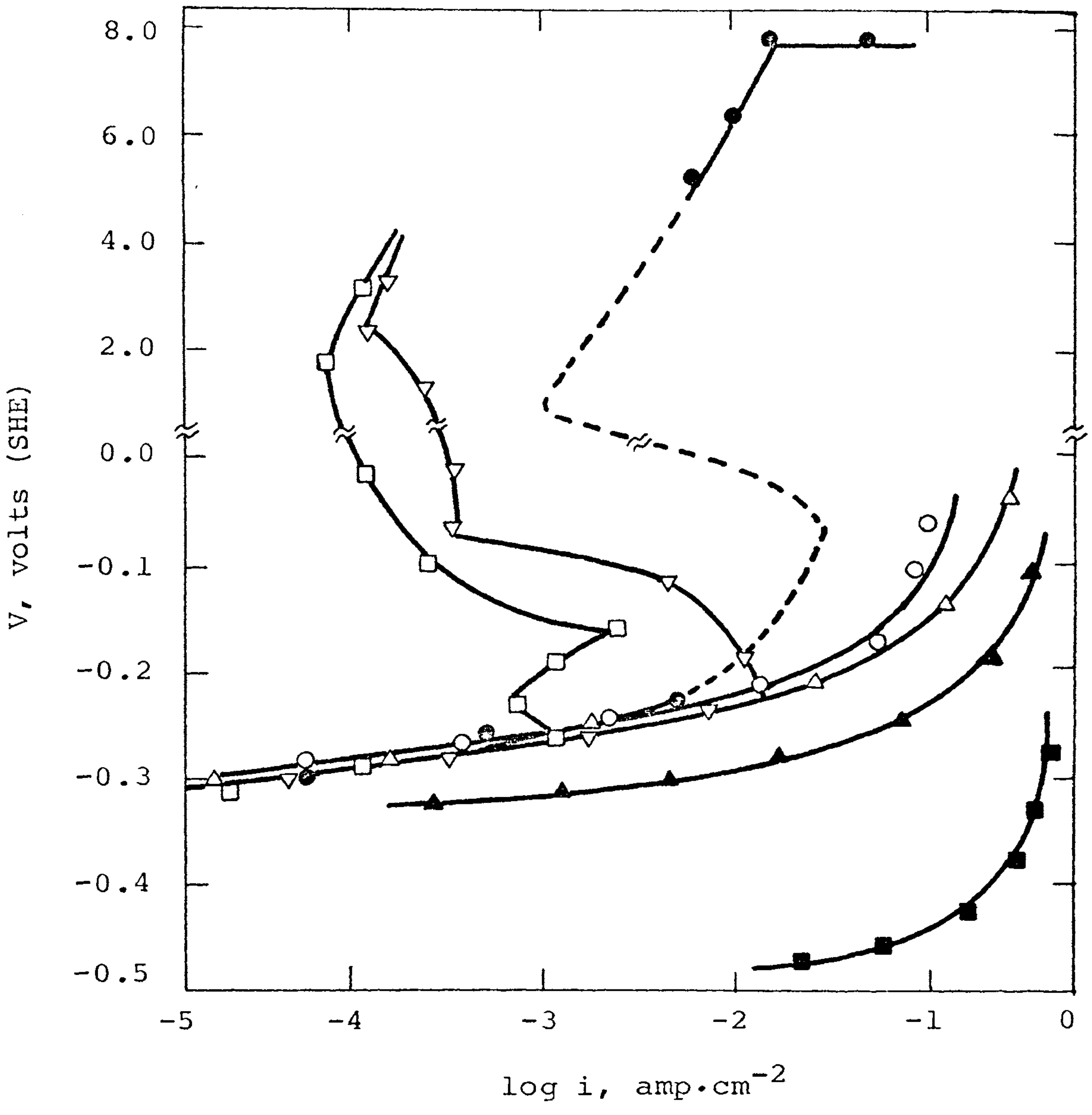

Fig. 1. Anodic polarization curves for the Sn electrode in acidic chloride solutions at 25°C.

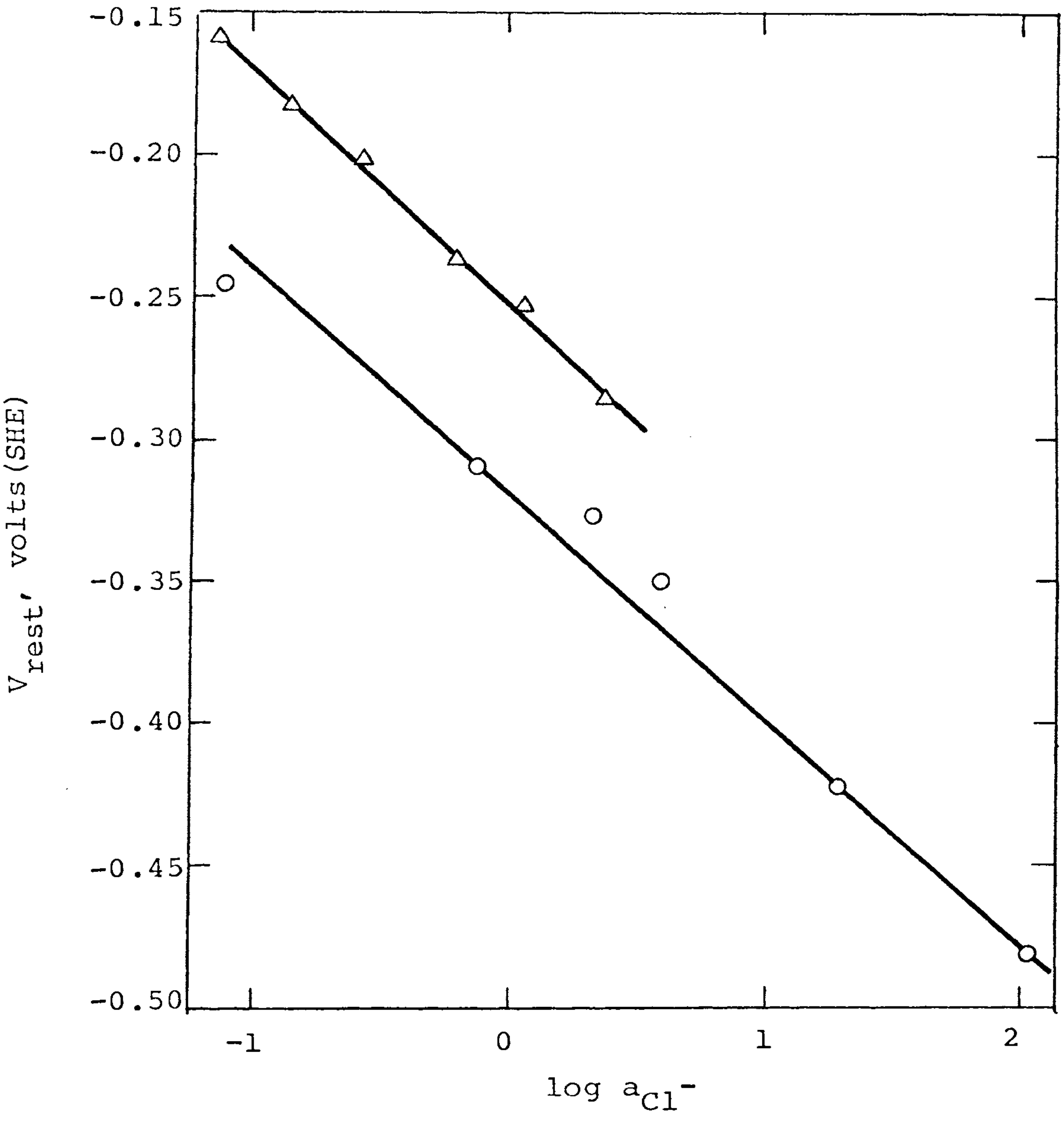

Fig. 2. Rest potential of the Sn electrode in chloride solutions at 25°C.

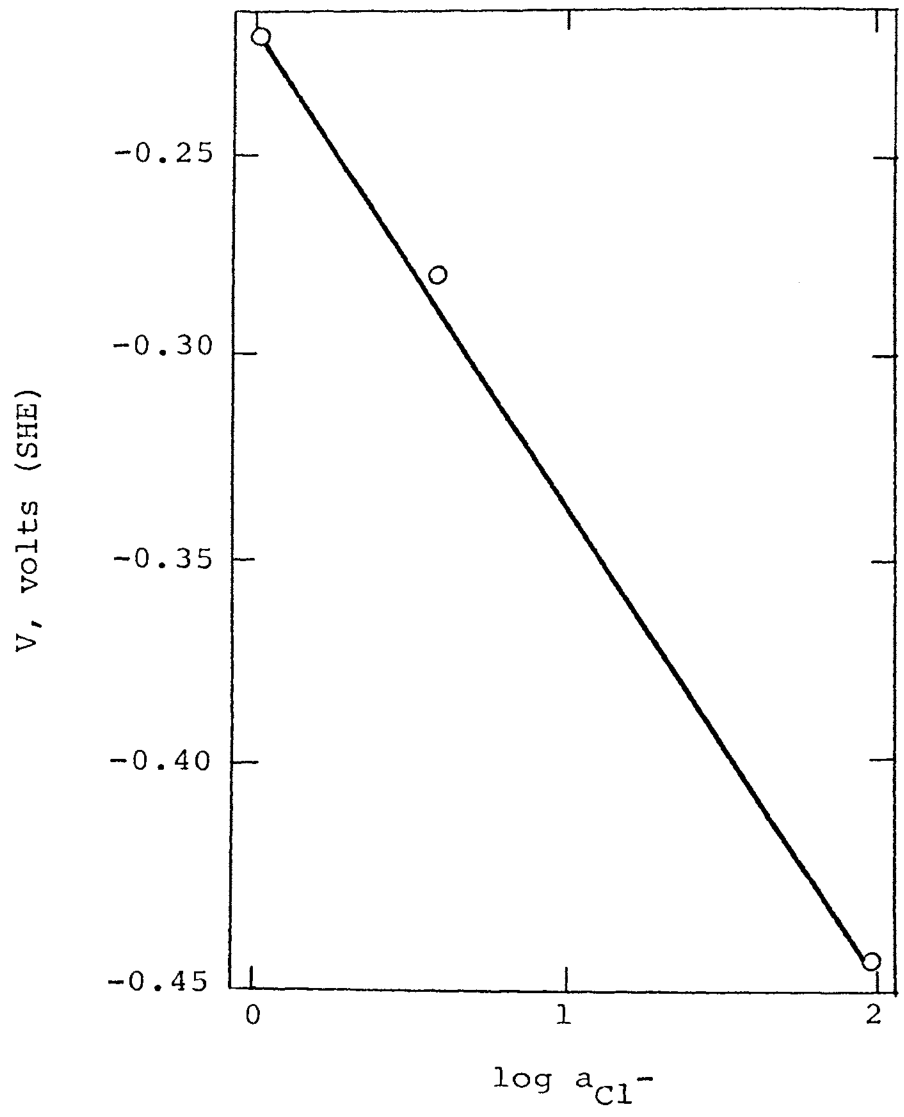

Fig. 3. Effect of Cl^- on the anodic dissolution of Sn at 25°C.

APPENDICES

APPENDIX A

Materials

The following is a list of the major materials used in this investigation.

1. Hydrochloric Acid. Reagent grade, meets ACS specifications. Fisher Scientific Co., New Jersey.
2. Potassium Chloride. Reagent grade, meets ACS specifications. Mallinckrodt Co., New York.
3. Nitrogen. Prepurified grade, Matheson Co., Joliet, Illinois.
4. Tin. Three inch bar, 99.999% purity. Electronic Space Products Inc., Los Angeles, California.

APPENDIX B

Equipment

The following is a list of the principal equipment components used in this investigation.

1. Surface Preparation of Tin Specimens.
    a. Belt surfacer. Buehler No. 1250. Buehler Ltd., Evanston, Illinois.
    b. Hand Grinder. Handimet, 4 stage, Buehler No. 1470, Buehler Ltd., Evanston, Illinois.
2. Electrolysis Apparatus.
    a. Power supply. Model 500R Serial A-1493, Kepco Laboratories, Inc., Flushing, New York.
    b. Electrometer. Model 610B, Keithy Instruments, Inc., Cleveland, Ohio.
    c. Ammeter. Ultra high sensitivity volt-ohm-micro-ammeter, Simpson 269, Simpson Electric Co., Chicago, Illinois.
    d. Power resistor. Model 931, Weston Electric Instruments Cor., Newark, New Jersey.
    e. Potentiostat. Anotrol, Model 4100, Anotrol Division of Continental Oil Co., Ponca City, Oklahoma.
    f. Strip Chart Recorder. Model 7100A. Autograph F.L. Moseley Co., Pasadena, California.

g. pH meter. Model 19, Fisher Scientific Co., Pittsburgh, Pennsylvania.

h. Balance. Type 2604, Sartorius-Werke Co., Germany.

APPENDIX C

TABLE II

X-RAY DIFFRACTION DATA FROM THE BLACK FILM FORMED DURING THE ANODIC DISSOLUTION OF Sn AT 25°C*

Experimental Values ("d" Spacings, A°)	A.S.T.M. Values for SnO	A.S.T.M. Values for $2SnO \cdot H_2O$
4.82	4.85	
2.87	2.98	
2.51	2.68	
1.92	1.90	
3.59		3.53
3.37		3.32
3.07		2.99
2.81		2.82
2.47		2.40

*In 0.01 N HCl - 0.99 KCl mixture.

APPENDIX D

Current Potential Data

TABLE III

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF Sn IN 10 N HCl (pH = -2.0) AT 25°C

E volts (NCE)	E* volts (SHE)	$i \times 10^{-3}$** amp	$i \times 10^{-3}$ $amp \cdot cm^{-2}$
0.75	-0.48	0.0	
0.74	-0.47	22.0	21.5
0.73	-0.46	59.0	57.7
0.72	-0.45	91.0	89.0
0.71	-0.44	123	120
0.70	-0.43	170	166
0.68	-0.41	230	225
0.65	-0.38	300	293
0.60	-0.33	370	362
0.55	-0.28	430	420

---

*$E = E_{ref} - E_m + E_j$, where $E_{ref} = 0.28v$, $E_j = 0.011v$

**Area of the electrode = 1.02 cm^2.

TABLE IV

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF Sn IN 3 N HCl (pH = -0.6) at 25°C

E volts (NCE)	E* volts (SHE)	$i \times 10^{-3}$** amp	$i \times 10^{-3}$ $amp \cdot cm^{-2}$
0.650	-0.35	0.0	0.0
0.625	-0.325	0.27	0.28
0.620	-0.32	0.58	0.60
0.615	-0.315	1.15	1.19
0.610	-0.31	2.10	2.17
0.605	-0.305	3.10	3.20
0.600	-0.300	4.20	4.35
0.590	-0.29	7.60	7.85
0.580	-0.28	17.0	17.6
0.570	-0.27	33.5	34.6
0.560	-0.26	52.0	53.8
0.550	-0.25	69.5	71.8
0.540	-0.24	89.0	92.0
0.520	-0.22	127	131
0.490	-0.19	210	217
0.450	-0.16	260	269
0.400	-0.11	320	331
0.320	-0.03	320	331

*$E = E_{ref} - E_m + E_j$ where $E_{ref} = 0.28v, E_j = 0.020$ v

**Area of the electrode = 0.968 cm^2.

TABLE V

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF Sn IN 1 N HCl (pH = 0.2) AT 25°C

E volts (NCE)	E* volts (SHE)	$i \times 10^{-3}$ ** amp	$i \times 10^{-3}$ $amp \cdot cm^{-2}$
0.618	-0.31	0.000	
0.610	-0.30	0.018	0.019
0.600	-0.29	0.056	0.058
0.590	-0.28	0.160	0.166
0.580	-0.27	0.310	0.321
0.570	-0.26	0.480	0.496
0.560	-0.25	1.75	1.82
0.540	-0.23	7.20	7.4
0.520	-0.21	25.0	25.8
0.490	-0.18	57.5	59.4
0.450	-0.14	115	119
0.400	-0.091	204	211
0.350	-0.041	255	264

*$E = E_{ref} - E_m + E_j$, where $E_{ref} = 0.28$ v, $E_j = 0.029$ v

**Area of the electrode = 0.968 cm^2.

TABLE VI

THE CURRENT-POTENTIAL REALTIONSHIP FOR THE ANODIC DISSOLUTION OF Sn IN 0.1 N HCl - 0.9 N KCl (pH = 1.2) AT 25°C

E volts (NCE)	E* volts (SHE)	$i \times 10^{-3}$** amp	$i \times 10^{-3}$ $amp \cdot cm^{-2}$
0.60	-0.315	0.000	
0.58	-0.295	0.025	0.024
0.57	-0.285	0.060	0.059
0.56	-0.275	0.180	0.176
0.55	-0.265	0.380	0.372
0.54	-0.255	1.00	0.980
0.53	-0.245	2.10	2.06
0.52	-0.235	3.70	3.62
0.51	-0.225	7.80	7.63
0.50	-0.215	14.4	14.1
0.49	-0.205	26.0	25.4
0.48	-0.195	36.0	35.2
0.46	-0.175	55.0	53.8
0.44	-0.155	70.0	68.5
0.40	-0.115	84.5	82.7
0.35	-0.065	94.0	92.0

*$E = E_{ref} - E_m + E_j$. where $E_{ref} = 0.28$ v, $E_j = 0.005$ v

**Area of the electrode = 1.02 cm^2.

TABLE VII

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF Sn IN 0.01 N HCl·0.99 N KCl (pH = 2.2) AT 25°C

volts (NCE)	volts (SHE)	$i \times 10^{-3}$ amp**	$i \times 10^{-3}$ $\text{amp}\cdot\text{cm}^{-2}$
0.60	-0.32	0.000	
0.59	-0.31	0.018	0.018
0.58	-0.30	0.049	0.048
0.57	-0.29	0.132	0.130
0.56	-0.28	0.330	0.322
0.55	-0.27	0.740	0.725
0.54	-0.26	1.60	1.57
0.53	-0.25	3.6	3.52
0.52	-0.24	7.5	7.35
0.51	-0.23	13.5	13.2
0.47	-0.19	10.6	10.4
0.44	-0.16	6.5	6.35
0.40	-0.12	4.3	4.20
0.35	-0.07	0.340	0.330
0.30	-0.02	0.360	0.352
0.20	0.08	0.390	0.382
0.00	0.28	0.300	0.294
-1.00	1.28	0.240	0.235
-2.00	2.28	0.120	0.115
-3.00	3.28	0.160	0.156

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*$E = E_r - E_m + E_j$, where $E_{ref} = 0.28$ v, $E_j = 0.0005$ v

**Area of the electrode = 1.02 cm^2.

TABLE VIII

THE CURRENT-POTENTIAL RELATIONSHIP FOR THE ANODIC DISSOLUTION OF Sn IN 0.001 N HCl-0.999 N KCl (pH = 2.9) AT 25°C

E volts (NCE)	E* volts (SHE)	$i \times 10^{-3}$ ** amp	$i \times 10^{-3}$ $amp \cdot cm^{-2}$
0.60	-0.32	0.000	
0.59	-0.31	0.024	0.024
0.58	-0.30	0.054	0.053
0.57	-0.29	0.115	0.113
0.56	-0.28	0.280	0.274
0.54	-0.26	1.15	1.13
0.52	-0.24	4.70	4.60
0.51	-0.23	0.730	0.715
0.50	-0.22	0.720	0.705
0.47	-0.19	1.10	1.08
0.44	-0.16	2.40	2.35
0.41	-0.13	1.70	1.66
0.38	-0.10	0.25	0.245
0.30	-0.02	0.110	0.108
0.20	+0.08	0.104	0.103
0.00	+0.28	0.069	0.068
-0.50	+0.78	0.031	0.030
-1.50	+1.78	0.080	0.079
-2.00	+2.28	0.092	0.090
-2.90	+3.18	0.120	0.117

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*$E = E_{ref} - E_m + E_j$, where $E_{ref} = 0.28$ v, $E_j = 0.000051$v

**Area of the electrode = 1.02 cm^2.

TABLE IX

THE CURRENT-POTENTIAL RELATIONSHIP (GALVANOSTATIC) FOR THE ANODIC DISSOLUTION OF Sn IN 0.001 N HCl - 0.999 N KCl (pH = 2.9) AT 25°C

E volts (NCE)	E* volts (SHE)	$i \times 10^{-3}$ ** amp	$i \times 10^{-3}$ $amp \cdot cm^{-2}$
0.60	-0.32	0.000	
0.59	-0.31	0.020	0.020
0.58	-0.30	0.060	0.060
0.56	-0.28	0.150	0.147
0.54	-0.26	0.500	0.490
0.53	-0.25	1.50	1.47
0.51	-0.23	5.00	4.90
-5.00	+5.28	6.00	5.87
-6.00	+6.25	10.0	9.80
-7.50	+7.75	16.0	15.6
-7.50	+7.75	50.0	49.0

* $E = E_{ref} - E_m + E_j$ where $E_{ref} = 0.28$ v, $E_j = 0.000051$v

** Area of the electrode = 1.02 cm^2.

APPENDIX E

TABLE X

CORRECTION FOR JUNCTION POTENTIAL BETWEEN HCl AND KCl SOLUTIONS USING EQUIVALENT CONDUCTANCE DATA

Solution, g-mole/l								
HCl	KCl	Λ	$\frac{\Lambda}{98.27}$	$\log \frac{\Lambda}{98.27}$	E_j	E_m	E_{Sn}^*	$\log A_{Cl^-}$
-	1	98.27	-	-	-	-	-	-
10^{-3}	0.999	98.47**	1.002	0.000848	+0.000051	0.60	-0.320	-
10^{-2}	0.99	100.3 **	1.021	0.00903	+0.0005	0.604	-0.323	-
10^{-1}	0.9	118.5 **	1.206	0.0813	+0.0048	0.595	-0.310	-
10^{-1}	-	351	3.572	0.5529	+0.033	0.56	-0.247	-1.099
1	-	301	3.063	0.4861	+0.029	0.618	-0.309	-0.092
2	-	254	2.585	0.4125	+0.024	0.63	-0.326	0.305
3	-	218	2.218	0.3460	+0.020	0.65	-0.350	0.598
6	-	128	1.303	0.1149	+0.0048	0.71	-0.423	1.28
10	-	64.4	0.655	-0.1838	-0.011	0.75	-0.481	2.02

*$E_{Sn} = E_{cal} + E_j - E_m$; where $E_{cal} = 0.280$ v; $E_j = 0.0591 \log \frac{\Lambda}{\Lambda_{KCl}}$ (for 1 N KCl); and E_m = measured potential.

**Molar average.

APPENDIX F

TABLE XI

ACTIVITY AND pH VALUES OF HCl AND KCl SOLUTIONS AT 25°C

Conc.	$\gamma_\pm$	log $\gamma_\pm$	a_{Cl^-} or a_{H^+}	log a_{Cl^-}	pH
0.1 HCl	0.796		0.0796	-1.09	1.09
1	0.809		0.809	-0.92	0.092
2	1.01		2.02	0.305	-0.305
3	1.32		3.96	0.598	-0.598
6	3.22	0.506	19.2	1.28	-1.28
10	10.44	1.021	105	2.02	-2.02
10^{-3} KCl	1		10^{-3}	-3.00	7.0
10^{-2}	0.901		0.00901	-2.045	7.0
0.1	0.769		0.0769	-1.11	7.0
0.2	0.717		0.1434	-0.843	7.0
0.4	0.67		0.268	-0.572	7.0
1.0	0.605		0.605	-0.218	7.0
2.0	0.575		1.15	+0.061	7.0
4.0	0.582	0.239	2.32	+0.367	7.0

*Calculated using the product of the mean ionic activity coefficient and the concentration.

VITA

Edward C. H. Liu was born in Tainan, Taiwan, on August 17, 1940. He received his elementary and high school education at Tainan, Taiwan. He entered Chung Yuan Christian College of Science and Engineering in 1959 and received a Bachelor of Science degree in Chemical Engineering in 1963.

After graduation, he served in the Chinese Army for one year as a second lieutenant. From November 1965 to December 1968, he worked as an engineer for Kaohsiung Oil Refinery, a subsidiary of Chinese Petroleum Corporation in Kaohsiung, Taiwan.

He came to the United States and enrolled in the Graduate School of the University of Missouri-Rolla in June 1968.